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Thiophene hydrodesulfurization over modified alumina-supported molybdenum sulfide catalysts

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Thiophene hydrodesulfurization (HDS), hexene-1 hydrogenation (HD) and water–gas shift (WGS) activities were measured over molybdenum-loaded catalysts supported on alumina modified with rare-earth oxides. MoS_2 supported on γ-Al_2O_3/La_2O_3 and γ-Al_2O_3/CeO_2 showed better performance in HDS and HD than on non-modified alumina, whereas better activity in the WGS reaction was only observed for catalysts supported on γ-Al_2O_3/CeO_2.

Keywords: Mo-loaded catalysts, hydrodesulfurization, water–gas shift reaction, rare-earth oxides

1. Introduction

Hydrodesulfurization (HDS) of oil fractions is one of the important refining processes. The importance is related to the increased demand to convert heavier and more sulfur-rich feedstocks as well as to the environmental pressure to reduce continuously the sulfur content in oil products. Therefore, there is a need for introduction of the so-called deep HDS process which will require new designs and new, more active catalysts.

In recent years much effort was concentrated on fundamental research between the reactivity and structure [1–4] of typical alumina-supported Co–Mo–S and Ni–Mo–S catalysts. It was established for transition metal sulfides (TMS) and specifically for Mo-based systems that the metal–sulfur binding energy is one of the main factors determining activity [5–7]. The importance of Mo–S bonds in catalysis has its origin in the unique chemistry of molybdenum ions with sulfur ligands. The diversity in structural and reactivity characteristics of Mo–S compounds derives mainly from the close matching of S 3p and Mo 4d orbital energies that provide low energy super-exchange pathways for intramolecular electron transfer processes.

The influence of the support, however, in these transformations cannot be neglected. Works by Knözinger [8], Daly [9] and Wang [10] indicate that structure as well as electronic properties of the support influence the catalytic processes with supported TMS catalysts.

This paper seeks to contribute to a better understanding of the support influence on catalytic activity in three catalytic processes (hydrodesulfurization (HDS), hydrogenation (HD) and water–gas shift (WGS)) applying alumina modified with rare-earth oxides as the support and sulfided Mo as the active phase.

2. Experimental

Two series of alumina-supported catalysts containing 8 wt% Mo were obtained from γ-alumina containing La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3 and Sm_2O_3. γ-alumina used in this study was prepared by hydrolysis of aluminum isopropoxide at 335 K. The obtained bohemite was calcined at 825 K in air and next impregnated at room temperature with an appropriate amount of lanthanide nitrate dissolved in ethanol, followed by evaporation to dryness and calcination at 825 K in air. In all cases the amount of the rare-earth oxide was either 1 or 4 wt%. More details of the support preparation can be found elsewhere [11]. Molybdenum was introduced by the "incipient wetness" method from a solution of ammonium heptamolybdate ($pH = 7.55$). After drying at ambient temperature and 385 K (16 h) samples were next activated for 16 h at 825 K in air.

Catalytic activities in hydrodesulfurization of thiophene, hydrogenation of hexene-1 and water–gas shift reaction were measured under atmospheric pressure in a fixed-bed reactor connected to an on-line gas chromatograph. The catalyst weight for HDS and HD reactions was 0.25 g. Prior to the catalytic reaction the catalysts were sulfided for 2 h at 675 K in a flow of a mixture of 10 vol% H_2S in H_2. After cooling to 625 K in a stream of helium the feed containing 2 vol% of thiophene or hexene-1 flowing at a rate of 50 $cm^3\,min^{-1}$ was directed onto the catalyst bed. The WGS reaction was performed at 625 K. Catalyst samples weighing 0.5 g were sulfided at 675 K for 2 h prior to the WGS tests. The $H_2O:CO$ ratio was kept at 1. The gaseous feed (49 vol% H_2, 49 vol% CO and 2 vol% H_2S) saturated with water vapour entered the reactor at a rate of 50 $cm^3\,min^{-1}$. More details related to the measurement of water–gas shift reaction activities are given elsewhere [12]. BET surface area and pore size distribution of non-sulfided supports were measured using a Micromeritics ASAP 2010

Table 1
Surface area and porosity of applied supports.

Support	BET surface area ($m^2\,g^{-1}$)	Average pore radius[a] (Å)	Pore volume[a] ($cm^3\,g^{-1}$)
γ-Al_2O_3	233	26	0.38
γ-Al_2O_3 + 1 wt% La_2O_3	250	29	0.44
γ-Al_2O_3 + 1 wt% CeO_2	242	26	0.39
γ-Al_2O_3 + 1 wt% Pr_6O_{11}	242	30	0.45
γ-Al_2O_3 + 1 wt% Nd_2O_3	240	32	0.44
γ-Al_2O_3 + 1 wt% Sm_2O_3	241	30	0.45
γ-Al_2O_3 + 4 wt% La_2O_3	275	29	0.47
γ-Al_2O_3 + 4 wt% CeO_2	257	26	0.40
γ-Al_2O_3 + 4 wt% Pr_6O_{11}	277	28	0.46
γ-Al_2O_3 + 4 wt% Nd_2O_3	278	28	0.47
γ-Al_2O_3 + 4 wt% Sm_2O_3	260	30	0.48

[a] Measured from the desorption curve.

Table 2
Catalytic activity of catalysts containing 8 wt% of Mo after 2 h of reaction.

Support applied	HDS of thiophene K ($cm^3\,s^{-1}\,g^{-1}$)	HD of hexene-1 K ($cm^3\,s^{-1}\,g^{-1}$)	WGS K ($cm^3\,min^{-1}\,g^{-1}$)	NO adsorption ($cm^3\,g^{-1}$)
γ-Al_2O_3	0.16	0.79	47.07	1.20
γ-Al_2O_3 + 1 wt% La_2O_3	0.30	0.75	41.57	1.50
γ-Al_2O_3 + 1 wt% CeO_2	0.28	0.89	52.07	1.36
γ-Al_2O_3 + 1 wt% Pr_6O_{11}	0.14	0.86	46.65	2.10
γ-Al_2O_3 + 1 wt% Nd_2O_3	0.13	0.78	44.25	1.35
γ-Al_2O_3 + 1 wt% Sm_2O_3	0.12	0.86	48.51	1.78
γ-Al_2O_3 + 4 wt% La_2O_3	0.08	1.03	60.92	1.22
γ-Al_2O_3 + 4 wt% CeO_2	0.10	0.93	72.64	1.74
γ-Al_2O_3 + 4 wt% Pr_6O_{11}	0.11	0.76	58.92	1.39
γ-Al_2O_3 + 4 wt% Nd_2O_3	0.10	0.84	54.82	1.75
γ-Al_2O_3 + 4 wt% Sm_2O_3	0.08	0.69	48.83	0.96

apparatus. Average pore radius (0.85–150 nm) was calculated from the desorption curve applying the BJH method. An atmospheric flow pulse technique was used to measure NO adsorption at 275 K. Pulses of NO ($\sim$1 cm^3) were introduced into the He stream, passing over the sulfided sample, every 3 min until no further adsorption was noted. Corrections for the contributions from the supports were made in blank experiments [13].

3. Results and discussion

It is well known from the literature [14] that addition of lanthanide oxides into γ-alumina significantly stabilize surface properties of this oxide at elevated temperatures. Recently it was established that formation of lanthanum aluminate [15], with a perovskite structure on the alumina surface is responsible for the retardation of sintering processes.

In our study, after modifying γ-alumina with small amounts (1 and 4 wt%) of rare-earth oxides, we observed an increase of surface area and consequently higher porosity of the studied samples. Data shown in table 1 indicate that after insertion of 1 wt% of lanthanide oxide, the surface area of γ-alumina increases of about 4–5% independently from the rare-earth element applied. A further increase of the surface area of γ-alumina was observed for the samples containing up to 4 wt% (total increase of $S_{\rm BET}$ was about 16%). Higher concentrations of lanthanide oxides caused only negligible changes.

A comparison of data given in table 1 with the results shown in figures 1 and 2 allows us to explain the increase of surface area after insertion of lanthanide oxide. Results shown in figures 1 and 2 for Al_2O_3/Nd_2O_3, being typical of all rare-earth oxides studied, clearly show formation of a secondary porous system which can be attributed to the surface lanthanide aluminate species [15]. Unfortunately, the concentrations of lanthanide oxides were not high enough to allow the detection of these surface species with ordinary X-ray diffraction measurements.

A secondary porous system, which in the case of pure γ-alumina is rather small, was observed in all samples studied. However, this porous system was the highest for samples containing Nd_2O_3, La_2O_3 and Sm_2O_3 and the lowest for CeO_2. For CeO_2, formation of the cerium aluminate is very much limited due to the absence of significant amounts of Ce^{3+} ions during preparation.

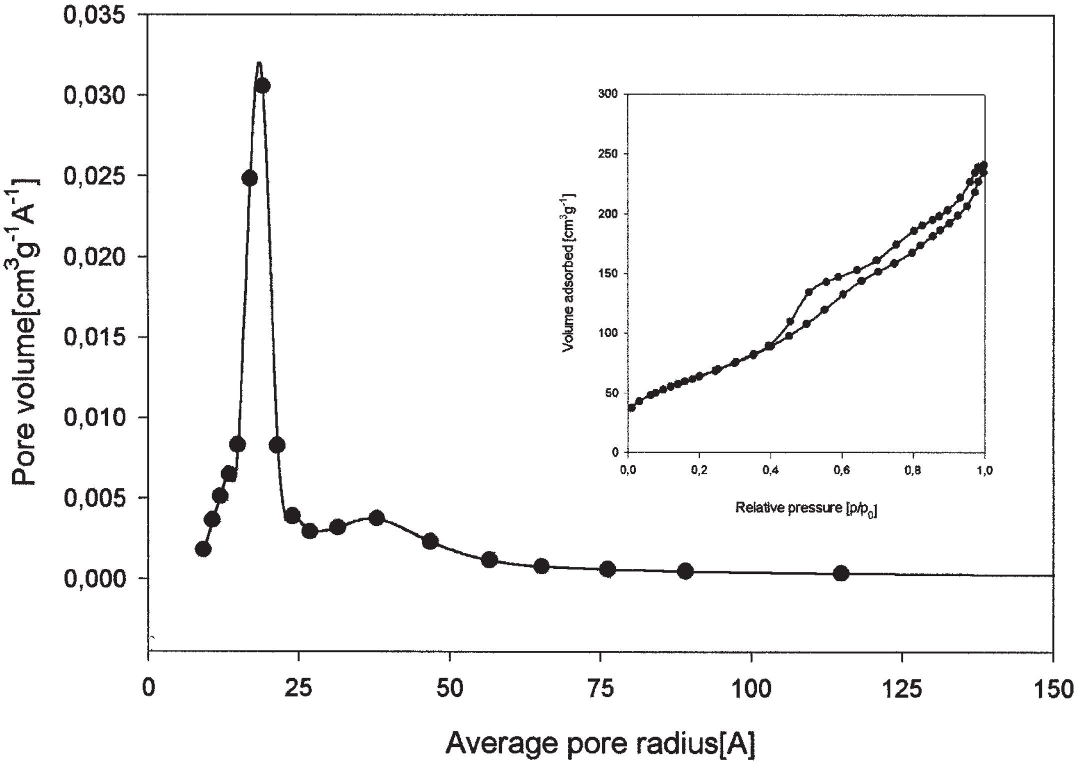

Figure 1. Pore size distribution in γ-Al_2O_3. Insert: isotherm of N_2 adsorption.

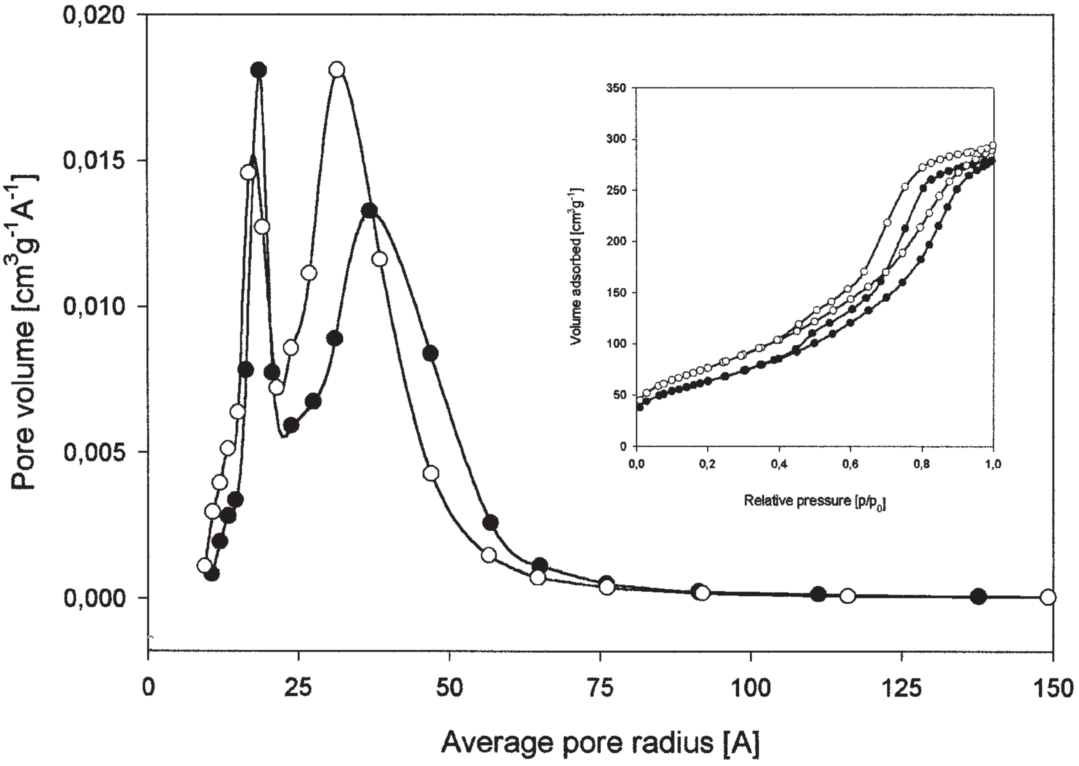

Figure 2. Pore size distribution in γ-Al_2O_3–1% Nd_2O_3 (filled circles) and γ-Al_2O_3–4% Nd_2O_3 (open circles). Insert: isotherms of N_2 adsorption.

The catalytic activities of the Mo-loaded catalysts prepared from the supports already described were tested in three reactions: hydrodesulfurization of thiophene, hydrogenation of hexene-1 and in the water–gas shift reaction. In these reactions the feed supplied to the catalyst bed always contained 2 vol% of H_2S and appropriate reagents. It was expected that sulfided Mo-loaded catalysts prepared from supports containing rare-earth elements, due to their higher surface area and different porous structure, will present better performance than analogous catalysts obtained from pure alumina. The data presented in table 2 agree only in some cases with our expectations, indicating that other factors rather than porous structure of the support play an important role. At this point it is worth pointing out that in all studied reactions we observed continuous deactivation with time. The data presented in table 2 collected after 2 h of reaction show values usually about 10–15% lower than initial ones. In the case of HDS reaction of thiophene only catalysts prepared from supports containing La and Ce showed higher activity than pure alumina–MoS_2. At higher concentration of rare-earth oxide in the support the activity after 2 h of reaction was much lower than for the pure alumina–MoS_2 system.

This is in contrast with the data obtained during hydrogenation of hexene-1, where higher concentration of lanthanide caused slight increases in catalytic activity. The results obtained show that these two reactions proceed on two different active sites. The active sites for hydrogenation are generated only at higher concentrations of lanthanide oxide in the support, whereas the active sites for HDS are formed on supports with low concentration of rare-earth oxide. In both cases, however, only supports doped with La_2O_3 and CeO_2 give better performance than pure alumina.

In the case of the water–gas shift reaction only catalysts derived from supports containing CeO_2 show better catalytic activity than pure alumina–MoS_2. These catalysts are more active with a higher concentration of CeO_2 in the support. Similar effects with other rare-earth oxides are less pronounced. The increased activity for Ce-containing catalysts can be explained by the relatively high reducibility of cerium ions to lower oxidation states. Similar effects were observed with TiO_2 when using it as a support for the WGS reaction [16].

No correlations between activity and NO sorption capacity were found for any of the studied samples and reactions. Results of NO adsorption shown in table 2 indicate a rather random distribution and a lack of any significant relation with activity. These observations lead us to the conclusion that NO adsorption at ambient temperatures, in contrast to the literature [17], is not a suitable method for measuring MoS_2 active sites, especially for lanthanide-oxide modified aluminas as supports. On the other hand, lack of the correlation between catalytic activity and active-phase dispersion, expressed here as NO adsorption capacity, indicates that the catalytic reaction proceeds not necessarily on the same sites as NO adsorption. However, due to the easy transformations of NO (e.g., oxidation and reduction) this technique for measuring a dispersion of the active phase can only be applied together with mass-spectroscopic measurements. Therefore, the gas-chromatographic method (hot-wire detector) for NO adsorption should be applied only in cases where both activity and NO adsorption are narrowly correlated.

The results of the present study show that γ-alumina modified with lanthanide oxides, used as support for MoS_2, changed the porous structure and surface area. However, higher surface area and changed porosity of modified γ-alumina do not influence significantly the activity in HDS, HD and WGS reactions. From CO_2 measurements on a series of Mo/Al_2O_3 catalysts of increasing Mo content Millman et al. [18] established that monolayer coverage with Mo species occurs at 8 wt% of Mo for alumina of 186 $m^2\,g^{-1}$. This was confirmed also by Zmierczak et al. [13]. In our experiments the surface area of the support always exceeded 200 $m^2\,g^{-1}$. Therefore our catalysts containing 8 wt% Mo were always below the limits of multilayer formation and in consequence also of different catalytic properties. Changes in activity for the lanthanide supports are related rather to the chemical nature of the surface than to surface area and porosity. However, no clear explanation for these effects was found at the moment.

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